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I, ANNA MAIJA MADL, ACTING TEAM LEADER EXAMINATION SUPPORT & SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 8738 for a patent by VICTORIA UNIVERSITY OF TECHNOLOGY filed on 17 February 1999.

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Eighth day of March 2000

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PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

**"ERASABLE/REWRITABLE OPTICAL DATA STORAGE WITH
PHOTOREFRACTIVE POLYMERS"**

Applicant:

VICTORIA UNIVERSITY OF TECHNOLOGY

The invention is described in the following statement:

ERASABLE/REWRITABLE OPTICAL DATA STORAGE WITH PHOTOREFRACTIVE POLYMERS

This invention relates to optical data storage and more particularly to erasable/rewritable three-dimensional optical data storage with photorefractive
5 polymers.

Multi-layered (or three-dimensional) optical memories have increasingly become a field of interest in the development of high-density optical data storage devices. Systems that utilise multiple layer recording can achieve recording densities from 100 to 10,000 times higher than conventional optical data storage
10 devices.

The use of two-photon excitation in three-dimensional (3D) bit optical data storage has grown due to its ability to increase the density in a given material by reducing the volume of the recorded bit. The probability of two-photon excitation is proportional to the squared intensity of the incident light; this effect produces
15 excitation only within a small region of the focus spot. As a result there is less cross talk between neighbouring data layers. Another advantage of two-photon excitation is the use of infrared illumination, which results in the reduction of scattering and enables the recording of layers at a deeper depth in a thick material.

Over the years different materials have been used for 3D bit data storage
20 under two-photon excitation. Two-photon 3D bits recorded in photopolymerizable and photobleaching materials have demonstrated that recording densities could reach terabits per cubic centimeter; unfortunately both materials are not erasable. Photochromic materials that undergo a change in isomer states and photochromic polymers that produce a change in refractive-index upon two-photon excitation are
25 both erasable materials. Another type of material that is of considerable interest is photorefractive material. The photorefractive effect results in a modulation of the refractive-index at the point of focus induced by the spatial distribution of electric charges upon illumination.

It has been discovered that such a change in the refractive index in
30 photorefractive material may be reversed by illuminating the medium again with radiation to produce a uniform redistribution of the electric charges and erase the

recorded information. However, this has previously only been achieved in a photorefractive crystals, e.g. lithium niobate (LiNbO_3), which are expensive to manufacture.

It is therefore desirable to provide a method of writing and erasing optical
5 data in relatively inexpensive materials.

According to one aspect of the invention, there is provided a method of writing and erasing optical data comprising:

producing a beam of focusable, coherent light;

focussing the beam on a photorefractive polymeric material to cause two-
10 photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to record data; and

illuminating the material with radiation to erase the recorded data.

According to another aspect of the invention there is provided a method of writing and re-writing optical data in a photorefractive polymeric material
15 comprising:

focussing a beam of coherent light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to write data;

illuminating the material with radiation to erase the recorded data;

20 focussing another beam of coherent light on the photorefractive material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to re-write data in the photorefractive material.

Preferably, the photorefractive polymeric material used in the method is such
25 that illumination with electro-magnetic radiation in the ultraviolet (UV) or visible spectrum produces a redistribution of the spacial distribution of the electric charges forming the data bits to erase the recorded data. The photorefractive polymer is preferably arranged to absorb radiation in only a narrow band in the UV to visible region of the electromagnetic spectrum. Creating a narrow absorption band will
30 decrease the materials susceptibility to deterioration from the reading process or from incidental ultraviolet light (e.g. from sunlight).

The photorefractive material preferably includes a chromophore which provides absorption in the UV to visible region. The polymer may also be doped with a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum. In one preferred embodiment, the polymer comprises poly (N-vinylcarbazole) (PVK) which may be doped with the photosensitive material 2, 4, 7 – trinitro – 9 – fluorene (TNF), and the chromophore comprises 2, 5 – dimethyl – 4 – (p – nitrophenylazo) anisole (DMNPAA). The polymeric material may also include a plasticiser, such as N-ethylcarbazole, (ECZ) to reduce the glass transition temperature of the material.

10 In the present invention, recorded bits of data may be read by employing a confocal microscope and/or a differential interference contrast (DIC) microscope utilising a source of coherent light of a wavelength on the edge of or outside the absorption band of the photorefractive polymeric material.

According to a further aspect of the invention there is provided a
15 photorefractive polymeric material for use in a method of erasable optical data storage comprising a polymer and a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the photorefractive material is such as to enable the recording of bits of data by two photon excitation, the reading of the bits of data by a source of coherent light
20 on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band. Optionally, the polymer may also be doped with a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum, and a plasticiser may be added to reduce the glass transition temperature of the material.

25 Preferably, a new photorefractive polymeric material in accordance with the second aspect of the invention includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive polymeric material:

30 25% - 99.5% of a polymer, such as PVK;
0.5% - 60% of a chromophore, such as DMNPAA;

0% - 5% of a photosensitive material, such as TNF; and

0% - 40% of a plasticiser, such as ECZ.

A preferred embodiment of the present invention using a cheap photorefractive polymer as a recording material for rewritable/erasable 3D bit

5 ~~optical data storage under two-photon excitation to produce a high-density 3D~~

optical data storage system will now be described by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a graph showing the absorption curve of a photorefractive polymeric material for use in the present invention;

10 Figure 2 is a schematic diagram of a two-photon excitation microscope used to record and read 3D data bits in a photorefractive polymer;

Figure 3(a) is a 24 x 24 bit pattern of the letter "C" recorded by two-photon excitation in a photorefractive polymer upon its first reading;

Figure 3(b) is the same region after reading 500 times.

15 Figure 3 (c) is a 24 x 24 bit pattern of the letter "A";

Figure 3 (d) is the same region as Figure 3(c) after being exposed to UV illumination showing complete erasure of the recorded information;

Figure 4 shows recorded 24 x 24 bit patterns at different depths in the photorefractive polymer using two-photon excitation;

20 Figure 4(a) shows a first layer including letter "A";

Figure 4(b) shows a second layer including letter "B" and

Figure 4(c) shows a third layer including letter "C".

One example of a new photorefractive polymeric material that has been used to demonstrate rewritable/erasable 3D bit optical data storage is the polymer poly
25 (*N*-vinylcarbazole) (PVK) doped with the photosensitive material 2, 4, 7-trinitro-9-fluorenone (TNF) which provides absorption in the UV to visible region of the spectrum. The photorefractive material also included, as a chromophore, 2, 5-dimethyl-4-(*p*-nitrophenylazo)anisole (DMNPAA) which also provides absorption in the UV to visible region. In this experiment compared with previous experiments
30 the randomly orientated chromophores were not aligned by applying an electric field (poling) during polymerisation and operation. Poling of the material requires

the creation of a magnetic field across the surfaces of the polymer. Such a uniform magnetic field is difficult to maintain across the surface of a large polymer sample, increasing the complexity in fabricating the new photorefractive polymer. Finally *N*-ethylcarbazole (ECZ) was added to reduce the glass transition temperature of the material. One preferred concentration of the materials DMNPAA:PVK:ECZ:TNF

is 50:33:16:1 by percentage weight of the total weight of the photorefractive material although it will be appreciated that different proportions of the constituent materials may be used within the ranges specified above. Uniform films of thickness 100µm were fabricated by combining all the materials in a teflon cast then polymerising the PVK at a temperature of 90°C over 2 days. The resulting polymer block was cut and polished to produce the sample used in the experiments.

Figure 1 illustrates the absorption band of a 100µm thick sample of the new photorefractive polymeric material as detected in an Oriel UV-Vis spectrophotometer using a Xenon arc lamp source.

It is seen from Figure 1 that the maximum of the absorption band of the new material is within 400-600 nm. Therefore a laser beam of an infrared wavelength at 800 nm can be used in the recording process to produce two-photon excitation at 400 nm. Since the absorption band cuts off at a wavelength of 630 nm, a range of wavelengths from 630 nm to 750 nm can be chosen to read out the recorded photorefractive data bits without suffering from single-or two-photon excitation.

Referring to Figure 2, there is illustrated an optical system for two photon recording of bits of data and for reading the bits of data in the photorefractive polymeric material. The recording system comprises a laser (10), a mechanical shutter (11), linked to a computer (20), lenses (12, 13), a pin hole aperture (14), another aperture (16), and an objective lens (18). For reading, the system also includes a beam splitter (22), a further lens (24), another pin hole aperture (26) and a detector (28) also linked to the computer (20). A three-dimensional scanning stage (30) is provided for the mounting of the sample of photorefractive material (32). The scanning stage (30) is movable in the x, y and z directions under the control of the computer (20).

In the recording process, a Spectra-Physics Tsunami Ti:sapphire laser (10) was focused into the photorefractive polymer sample (32). In mode-locking operation the laser can produce an ultrashort pulsed beam with a pulse width of 80 fs and an average power of 800 mW. The wavelength of the laser was tuned to 800 nm, which corresponds to twice the wavelength of the maximum absorption from the sample. From the absorption curve in Figure 1, we can see that there will be no single-photon absorption at a wavelength of 800 nm, only the two-photon absorption can occur at a wavelength of 400 nm. The logic state of the recorded information was controlled by the mechanical shutter (11) linked to the computer (20). The recording material (32) was mounted upon a Melles Griot computer-controlled 3D translation stage (30). For recording a Zeiss Fluor objective (18) with a numerical aperture of 0.75 and a magnification factor of 20 was used.

For reading the change in refractive-index caused by the two-photon photorefractive effect an Olympus Fluo View microscope was employed and used in a differential interference contrast (DIC) mode. A He-Ne laser of wavelength 632.8 nm was coupled into the Fluo View for reading the recorded information, as the wavelength of 632.8 nm is on the edge of the absorption and causes minimal damage to the recorded information (see Fig. 1). To erase the recorded information the region of interest was illuminated with either the UV line of a mercury lamp or an Argon ion laser in the Fluo View microscope. In both the reading and erasing an Olympus UPlanAPO objective (18) with a numerical aperture of 0.7 and a magnification factor of 20 was used.

As a demonstration of the ability to record information as a change in refractive-index using two-photon excitation, Figures 3(a) and 3(b) show the measured change in refractive-index produced at the focus spots. In recording an average power of 5 mW at the focus spot was used to record the information. A pattern (the letter C) consisting of 24 x 24 bits was recorded in the sample. The bit separation was 3.2 μm , and the exposure time for each bit was 25 ms. In the reading process a laser beam of power less than 5 mW was scanned across the sample to produce the DIC image. Figure 3(b) shows the deterioration of the recorded information after having been scanned 500 times. The contrast of the

recorded bit in Figure 3(b) is 90% of that in Figure 3(a). This feature illustrates that there is a slight erasing of the information due to absorption of the light used for reading. The information recorded in Figure 3(c) used the same power and exposure time as used in Figure 3(a) and Figure 3(b). Figure 3(d) shows the same
5 ~~region as seen in Figure 3(c) after being exposed to the UV illumination for 1-2~~
seconds. The result shows the complete erasure of the previously recorded information.

Figure 4 demonstrates the ability of this system to record and read changes in refractive-index of multiple layers of information. Three layers of information were
10 recorded with a layer separation of 10 μm . Each layer consists of a pattern of 24 x 24 bits. The first layer, recorded near the surface contains a pattern of the letter "A". The second and third layers consist of the letters "B" and "C", respectively thus the achieved 3D data density was approximately 10 Gbits/cm³, which is comparable to that previously achieved in photochromic polymers, a
15 photorefractive crystal and photobleaching materials.

It will be seen from the above that the present invention provides an effective method of recording, reading, erasing and rewriting three dimensional data in relatively inexpensive photorefractive polymeric materials using two photon
20 excitation to record and re-write the data and illumination with radiation in the UV or visible region of the electromagnetic radiation to erase the recorded data.

It will also be appreciated that various modifications, alterations and improvements may be made to the preferred embodiment described above without departing from the scope and spirit of the present invention. Such modifications or improvements that are envisaged to increase the storage capacity of the system
25 include the following:

1. The compensation of small amounts of cross talk between the layers (see Figure 4) due to spherical aberration from the refractive-index mismatch between the recording material ($n = 1.75$) and the immersion medium ($n = 1$). The refractive-index mismatch results in an increase in the diffraction spot size at deeper
30 position of a volume recording medium. A variable tube length method for

compensation of this type of aberration may be used in the new photorefractive material.

2. Due to the low power illumination in this new material, a continuous wave (CW) laser beam may be used rather than a pulsed beam to produce two-photon excitation. ~~With the help of a 1.2 W CW laser diode, operated at a near-~~
infrared wavelength, a fast, low cost, compact, erasable two-photon 3D bit optical data storage system can be achieved.

3. Different photorefractive polymers may be used and the chemical properties of the materials may be modified to lead to an increase in the stability of the photorefractive polymer. By tailoring the absorption spectrum we can
10 determine the wavelength of light that will affect the material. Creating a narrow absorption band in the UV or visible region will decrease the materials susceptibility to deterioration due to irradiation from the reading process or from incidental UV light (i.e. sunlight).

15 4. Methods for reading and/or recording small changes in refractive-index are 4Pi microscopy and confocal microscopy. The 4Pi microscopy technique involves illuminating a volume medium from two opposite directions to produce a common focal spot. Both systems are sensitive enough to detect small changes in refractive-index (recorded bits) and stable enough to incorporate variable tube
20 length compensation and two-photon excitation by illumination with ultrashort pulse or CW lasers, with fibre delivery and detection.

DATED: 17 February 1999

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VICTORIA UNIVERSITY OF TECHNOLOGY

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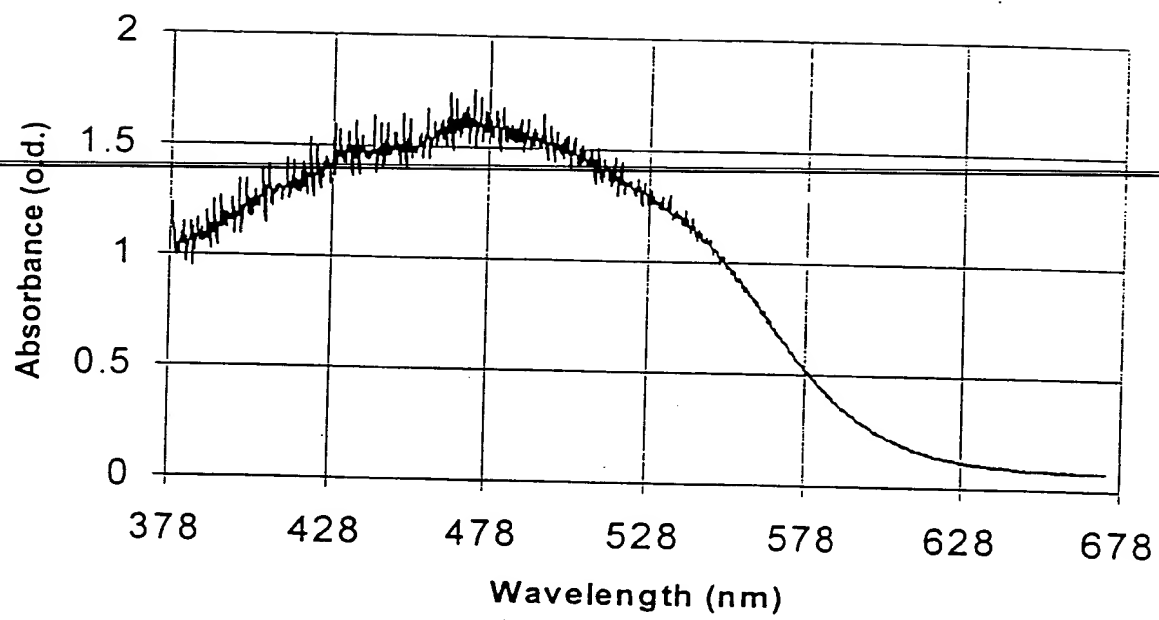


Figure 1.

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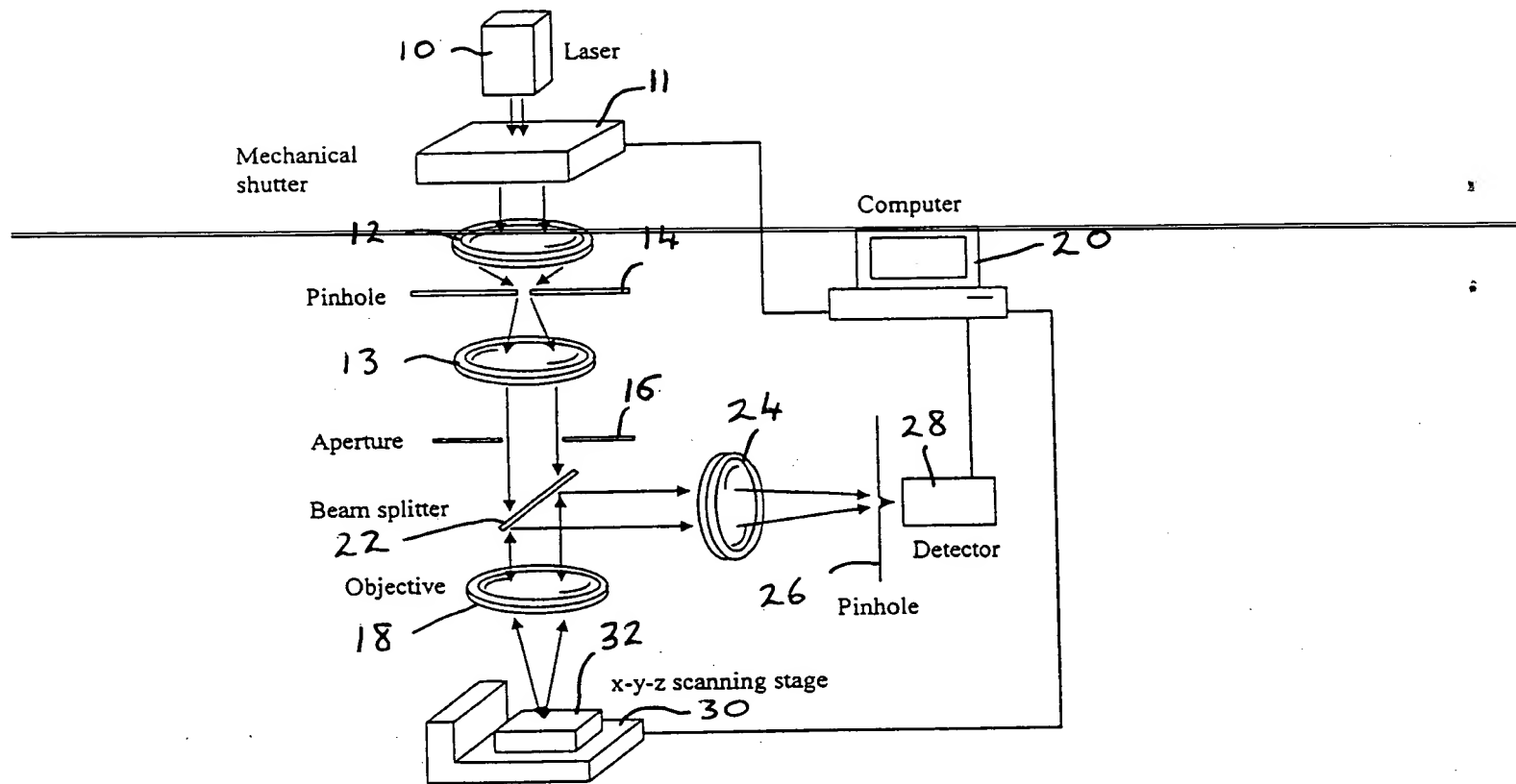
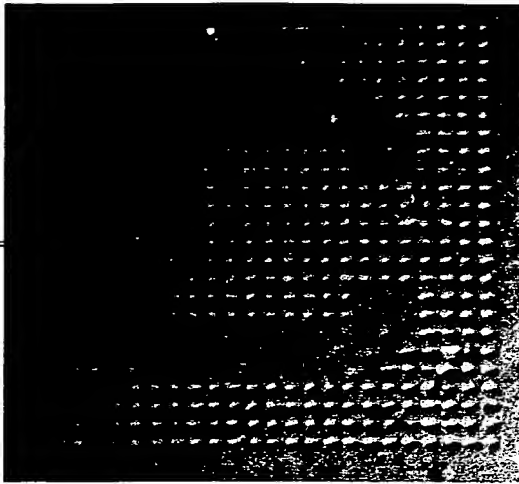
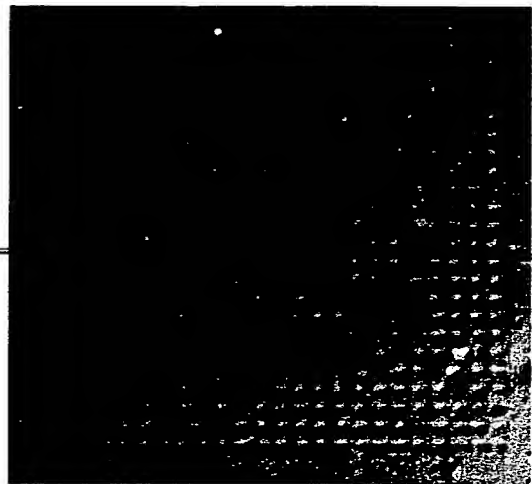


Figure 2.

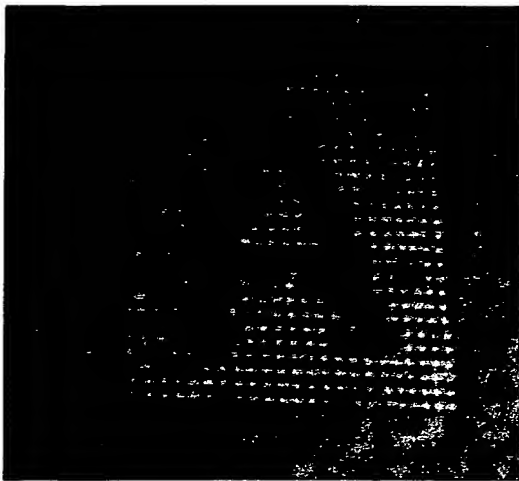
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(a)



(b)



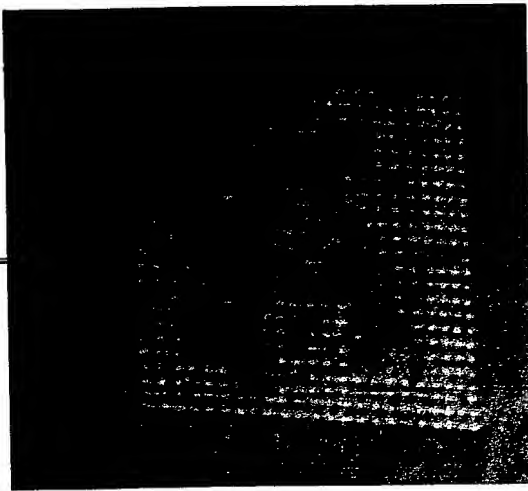
(c)



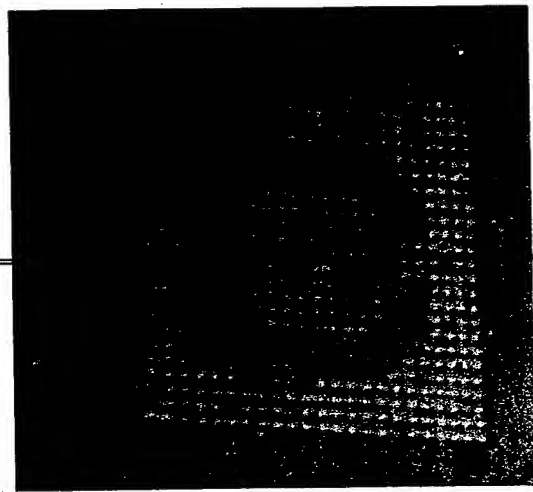
(d)

Figure 3.

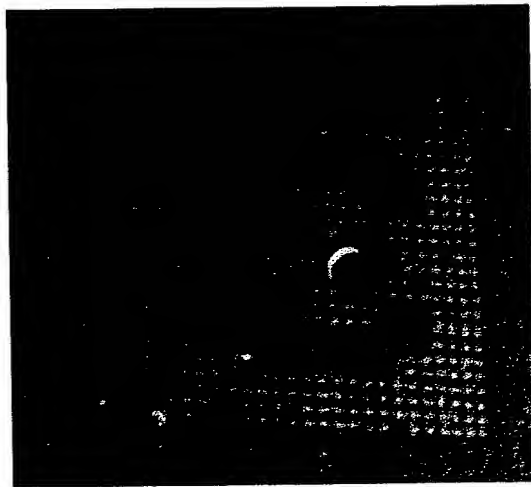
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(a)



(b)



(c)

Figure 4.